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LIQUID PHASE GROWTH OF $YBa_2Cu_3O_{7-x}$ AT LOW TEMPERATURES USING KOH FLUX

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Abstract

Molten KOH method, which was reported for the growth of $YBa_2Cu_4O_8$ (Y124) crystal, was applied to synthesize and grow $YBa_2Cu_3O_{7-x}$ (Y123) crystal. Y123 phase was synthesized by controlling growth temperature and oxygen partial pressure. The shape of synthesized grains was cubic-like, indicating that they grew by the transportation of solute through liquid phase. Using KOH flux method, substitution of rare-earth elements for Y in Y123 phase was easily obtained. Liquid phase epitaxy of Y123 film on a single crystalline substrate was achieved by slow cooling flux method but not by top-seeded solution growth yet.

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Keywords: Liquid phase epitasy; RE123; RE123; phase relation; film fabrication

1. Introduction

Epitaxial films of high-*T*c superconductor $REBa_2Cu_3O_{7-d}$ (RE123: RE denotes rare-earth element here after) are fabricated dominantly by vapor phase growth processes such as pulsed laser deposition. These processes provide not only good epitaxial structure but also magnetic pinning centers in the films. However, the growth rate of the films is not enough to produce superconducting cables in economically fast rate.

Liquid phase growth process such as top-seeded solution growth (TSSG) and liquid phase epitaxy (LPE) growth, which is recognized as a single crystal growth method, is able to give us a high quality crystalline film. For single crystalline bulk crystals and LPE films of RE123, BaO-CuO flux (so-called self flux) was used as a growth flux.

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BaO-CuO flux provides a high growth rate more than 10 μm/min. for RE123 growth. It was applied to the formation of RE123 films on various substrates even on textured metal substrates [1,2]. Crystalline defects and magnetic flux pinning centers in these films could be modified depending on the substrate used. The problem was that the process temperature was approximately 900°C, which was too high to produce a conductor with metal substrate.

Recently, new flux, molten KOH, was reported to be a growth flux for $YBa_2Cu_4O_8$ (Y124) phase [3]. The growth temperature was below 700°C, sufficiently low enough to use various substrate materials. Furthermore, it can grow Y123 phase at a low oxygen partial pressure [4]. In order to investigate processing potential of the KOH flux method for fabrication of RE123 and RE124 superconductors as a liquid phase growth process, this paper presents conditions growing Y123 and Y124 phases, morphology of obtained crystals and possibility of epitaxial growth on single crystalline substrates.

2. Experimental procedure

Starting materials of the solute used for the growth of RE123 and RE124 were RE_2O_3, $BaCO_3$ and CuO with the composition of the targeting phases. These materials were put in an aluminum crucible with the same weight of KOH of solvent and heated up to an adequate temperature in the ambient or regulated oxygen atmospheres. The crucible was kept at the temperature for about 10 hours for obtaining crystalline power. After being cooled down to room temperature, the synthesized crystalline powder was washed using water and ethanol. For growing these crystals on substrates, $NdGaO_3$ (NGO) single crystalline plates was settled in or dipped into the solution during the growth process.

3. Y123/Y124 phase boundary in temperature-pressure diagram

Equilibrium stable region of Y123 and Y124 phases are different in the diagram of temperature and partial pressure of oxygen ($P\mathrm{O}_2$) [5,6]. This means that it is quite reasonable that synthesis of Y123 and Y124 phases from KOH method can be controlled by controlling temperature and $P\mathrm{O}_2$. Therefore, obtained phases using KOH flux under different oxygen partial pressures and temperatures were determined by x-ray diffraction (XRD).

The growth experiment was performed in oxygen flow ($P\mathrm{O}_2$=1 atm), the ambient atmosphere ($P\mathrm{O}_2$=0.2 atm) and nitrogen flow ($P\mathrm{O}_2$=10^{-5} atom), whose oxygen pressure was measured by an oxygen analyzer. Composition of the metal elements in the starting materials was settled to be that of Y124 phase. Superconducting phases detected by XRD was summarized in a *p-T* diagram shown in Fig.1. Solid circle, open circle and square symbol denote Y123 Y124 and Y_2BaCuO_5 (Y211) phases, respectively. Cross symbol denotes no superconductor related phases or unreacted raw materials. At $P\mathrm{O}_2$ below 10^{-5} atm, only Y123 phase was synthesized between 500 and 750°C. At high $P\mathrm{O}_2$ and low temperature region Y124 phase was synthesized and clear phase boundary between Y123 and Y124 was observed. The border between Y123 and Y124 sifted toward high temperature as Po_2 increased.

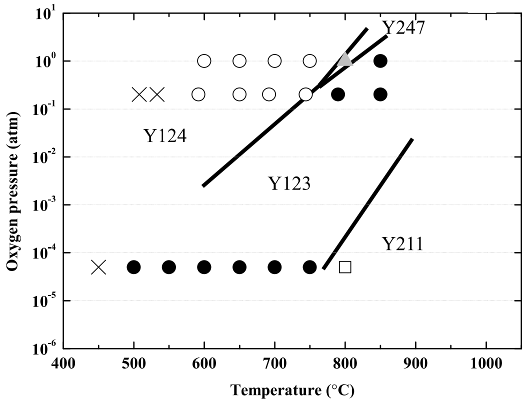

Fig. 1 *p-T* diagram showing generation region of superconducting phases in KOH system.

At the border temperature along P_{O_2}=1 atm, $Y_2Ba_4Cu_7O_{15}$ (Y247) phase (triangle) was detected in addition to Y123 and Y124 phases. It is determined that Y247 phase is stable between equilibrium regions of Y123 anY124 at P_{O_2} of about 1-10 atm by the solid state reaction system [5,6]. The formation of Y247 phase by the molten KOH method probably implies that equilibrium stable region of this phase exists between Y123 and Y124 regions at P_{O_2}=1 atm even in KOH containing system.

Phase relations obtained on the KOH involving system is similar to that for simple metal oxide system. However, KOH system sifted the border of Y123 and Y124 toward low temperature region or high Oxygen pressure region in *p*-*T* diagram.

4. RE-substitution of Y123 phase

RE substitution for Y in Y124 phase is simply obtained by KOH flux method. [7] In order to investigate RE-substitution of Y123 phase by KOH method, various rare-earth (La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er and Yb) oxides were substituted for Y_2O_3 in starting materials. All rare-earth substitutions for Y in Y123 investigated was easily synthesized at 700°C in N_2 gas flow except Ce. All synthesized RE123 phases showed good superconductivity except Pr123 phase. These results of phase formation and superconductivity are comparable with other preparation processes reported ever. Therefore, KOH flux method can be applied to the superconducting device fabrication process of RE123 and mixed RE123 phases.

5. Crystal morphology grown from KOH flux

Grains of crystalline Y123 and Y124 were observed by scanning electron microscopy. Fig.2 shows the morphology of these crystals grown at 600°C for Y123 and 650°C for Y124. Both phases show cubic-like shape surrounded by well-developed facet faces. The shape indicates that the growth of both Y123 and Y124 were governed by the surface diffusion mechanism and the solute transported through the liquid phase to the growing surfaces. The crystalline size was as small as at most 200μm and the Ostwald ripening did not proceed so much as the case of using BaO-CuO flux. This implies that the diffusion coefficient or the solubility of the solute in KOH flux is smaller than in BaO-CuO flux. However, it can be said that KOH flux method has a potential to be used as a liquid phase growth process for Y123 and Y124 film preparation.

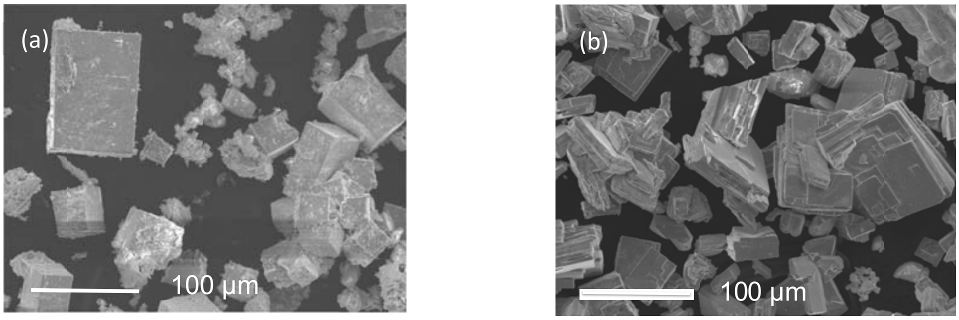

Fig. 2 Shape of the grown crystals of (a) Y123 and (b) Y124..

6. LPE growth of Y123 and Y124 by top-seeded solution growth

In order to apply liquid phase process to the fabrication of high-*T*c superconducting devices, LPE growth on a substrate is indispensable. To see the possibility of LPE film formation, a single crystalline NGO (001) substrate was settled in the raw material mixture and KOH flux growth was carried out with a slow cooling temperature profile. After the process the substrate was washed as the same manner for obtaining powder crystals. Depending on the growth conditions, i.e. temperature and atmosphere, Y124 or Y123 film grew on the substrate. XRD patterns shown in Fig. 3 indicated that both crystalline films grew c-axis oriented perpendicular to NGO (001) substrate.

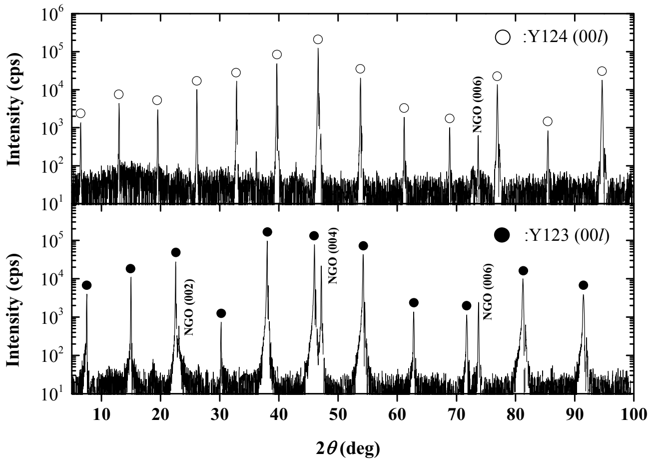

Fig. 3 XRD patterns of Y124 (upper) and Y123 (lower) grown on NGO substrate from molten KOH flux.

TSSG method is one of the simplest ways to detect the condition of the solution, which controls the quality of grown films to be applicable to various superconducting devices. Therefore, we tried it by dipping a substrate into the solution. Depending on temperature and atmosphere, we confirmed change of solution state, however, LPE film formation has not been achieved by TSSG method yet. This is probably due to inadequate composition of the system and temperature gradient.

7. Conclusion

According to the shape of grains grown by KOH flux method, it is confirmed that not only RE124 but also RE123 are grown from liquid phase. The growth conditions of the KOH growth were distinctly different for these two phases. Y124 was stable in a high $P\mathrm{O_2}$-low temperature region and Y123 was vice versa. Rare-earth substitution for Y in Y123 crystal was also easy by using KOH flux method. C-axis oriented LPE growth of Y123 and 124 films on single crystalline $NdGaO_3$ (100) was achieved.

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